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Iron Precatalysts with Bulky Tri(*t*-butyl)cyclopentadienyl Ligands for the Dehydrocoupling of Dimethylamine-Borane

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Abstract

In an attempt to prepare new Fe catalysts for the dehydrocoupling of amine-boranes and to provide mechanistic insight, the paramagnetic Fe^{II} dimeric complex [Cp'FeI]₂ (**1**) (Cp' = η⁵-(1,2,4-*t*-Bu)₃C₅H₂) was used as a precursor to a series of cyclopentadienyl Fe^{II} and Fe^{III} mononuclear species. The complexes prepared were [Cp'Fe(η⁶-Tol)][Cp'FeI₂] (**2**) (Tol = C₆H₅Me), [Cp'Fe(η⁶-Tol)][BAR^F₄] (**3**) (BAR^F₄ = [B(C₆H₃(*m*-CF₃)₂)₄]⁻), [N(*n*-Bu)₄][Cp'FeI₂] (**4**), Cp'FeI₂ (**5**), and [Cp'Fe(MeCN)₃][BAR^F₄] (**6**). The electronic structure of the [Cp'FeI₂]⁻ anion in **2** and **4** was investigated by SQUID magnetometry, EPR spectroscopy and *ab initio* Complete Active Space Self Consistent Field –Spin Orbit (CASSCF-SO) calculations, and the studies revealed a strongly anisotropic *S* = 2 ground state. Complexes **1-6** were investigated as catalysts for the dehydrocoupling of Me₂NH•BH₃ (**I**) in THF at 20 °C to yield the cyclodiborazane product [Me₂N–BH₂]₂ (**IV**). Complexes **1-4** and **6** were active dehydrocoupling catalysts towards **I** (5 mol % loading), however **5** was inactive, and ultra-violet (UV) irradiation was required for the reaction mediated by **3**. Complex **6** was found to be the most active precatalyst, reaching 80% conversion to **IV** after 19 h at 22 °C. Dehydrocoupling of **I** by **1-4** proceeded *via* formation of the aminoborane Me₂N=BH₂ (**II**) as the major intermediate, whereas for **6** the linear diborazane Me₂NH–BH₂–NMe₂–BH₃ (**III**) could be detected, together with trace amounts of **II**. Reactions of **1** and **6** with Me₃N•BH₃ were investigated in an attempt to identify Fe-based intermediates in the catalytic reactions. The σ-complex [Cp'Fe(MeCN)(κ²-H₂BH•NMe₂H)][BAR^F₄] was proposed to initially form in dehydrocoupling reactions involving **6** based on ESI-MS (ESI = Electrospray Ionisation Mass Spectroscopy) and NMR spectroscopic evidence. The latter also suggests that these complexes function as precursors to iron hydrides which may be the true catalytic species.

Introduction

Although catalytic transformations involving the formation of C–C or C–E (E = heteroatom) bonds have been extensively developed, the analogous creation of homonuclear and heteronuclear bonds between p-block elements are relatively unexplored.^{1–4} The potential for a range of applications for the resulting molecular and macromolecular main group species has helped stimulate the expansion of the field in recent years.^{5,6} In particular, the catalytic dehydrocoupling of amine- and phosphine-boranes has become a field of rapid growth over the past decade.^{4,7,8} This has largely been due to the potential of these compounds as hydrogen-storage materials,^{9,10} reagents for transfer hydrogenations and reductions of organic substrates,^{11–14} and as precursors to new inorganic polymeric and solid-state materials.^{15–20}

Many precatalysts have been reported for the dehydrogenation of amine-boranes, although the majority are based on expensive 4d or 5d elements.⁸ Inexpensive and abundant alternatives have recently been targeted, with systems based on Fe being of particular interest (**Figure 1**).^{21–41} The first example $\text{FeH}(\text{PMe}_2\text{CH}_2)(\text{PMe}_3)_3$ (**Figure 1, A**), was briefly reported by Baker and coworkers in 2007 and achieved high conversion of $\text{NH}_3\cdot\text{BH}_3$ to oligomeric material, using 10 mol% catalyst after 4 days in THF at 20 °C.²⁷ Subsequently, a series of complexes was reported by the same group, $\text{Fe}(\text{PCy}_3)(\text{N}(\text{SiMe}_3)_2)_2$, $\text{Fe}(\text{DEPE})(\text{NSiMe}_3)_2$ (DEPE = 1,2-bis(diethylphosphino)ethane, Cy = Cyclohexyl), (**Figure 1, B**).³¹ In 2011 we reported preliminary results on the use of a Fe^{I} complex $[\text{CpFe}(\text{CO})_2]_2$ (**Figure 1, C**) as a precatalyst for the catalytic dehydrogenation of $\text{NH}_3\cdot\text{BH}_3$ on photoirradiation at 20 °C over 4 h in THF.³² This Fe species represented a rare, early example of an amine-borane dehydrocoupling precatalyst to show significant activity at ambient temperature toward a range of amine-boranes, including substrates derived from primary and secondary amines as well as ammonia-borane.

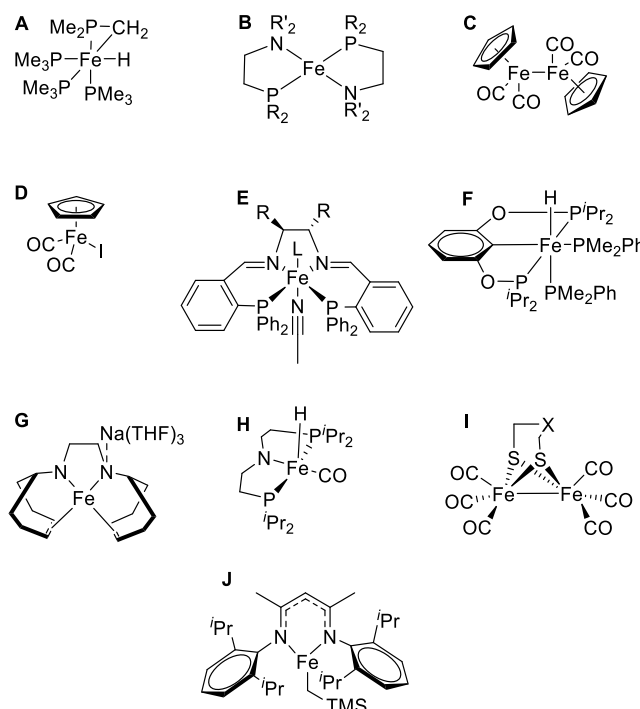
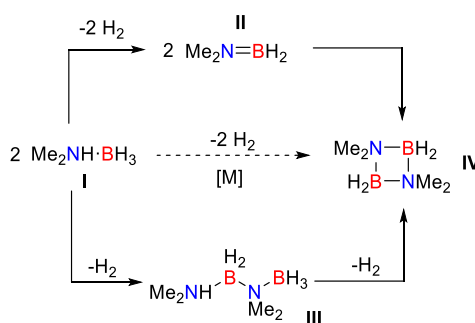
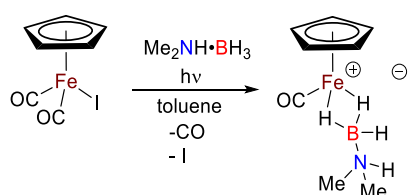


Figure 1. Overview of Fe based precatalysts reported to dehydrocouple amine-boranes.

In 2014 we reported a detailed further study of a range of Fe^{I} and Fe^{II} cyclopentadienyl carbonyl complexes as precatalysts. Upon irradiation with UV light, evidence was provided that the Fe^{I} complex $[\text{CpFe}(\text{CO})_2]_2$ reacted with $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (**I**) to generate small Fe nanoparticles (< 10 nm), which were proposed to be the catalytically active species in the dehydrocoupling of **I**.³³ However in contrast, the catalytic reaction with the Fe^{II} complex $\text{CpFe}(\text{CO})_2\text{I}$ (**Figure 1, D**) under photoirradiation was found to proceed *via* a homogeneous mechanism. The major intermediate in the dehydrocoupling reactions differed upon changing precatalyst; specifically, the reaction proceeded almost exclusively *via* **II** or **III** when precatalysts $[\text{CpFe}(\text{CO})_2]_2$ or $\text{CpFe}(\text{CO})_2\text{I}$ were used, respectively (**Scheme 1**).³³ Initial dissociation of CO and I from $\text{CpFe}(\text{CO})_2\text{I}$ was proposed to allow formation of the active species, a σ -borane Fe complex, and to enable subsequent dehydrocoupling (**Scheme 2**).³³ Modelling the reaction by density functional theory (DFT) led to the proposal of a mechanism that included an amine-borane σ -complex of the type $[\text{CpFe}(\text{CO})(\kappa^2\text{-H}_2\text{BH}\cdot\text{NHMe}_2)]^+$ as an intermediate.³³



Scheme 1. Dehydrogenation of $\text{Me}_2\text{NH}\cdot\text{BH}_3$ (**I**) to yield $[\text{Me}_2\text{N}-\text{BH}_2]_2$ (**IV**), highlighting the two major intermediates $\text{Me}_2\text{N}=\text{BH}_2$ (**II**) and $\text{Me}_2\text{NH}-\text{BH}_2-\text{NMe}_2-\text{BH}_3$ (**III**).



Scheme 2. Proposed intermediate for the dehydrocoupling of **I** by $[\text{CpFe}(\text{CO})_2\text{I}]$.

A series of Fe^{II} precatalysts of the general formula $[\text{Fe}(\text{NCMe})(\text{L})(\text{Ph}_2\text{C}_6\text{H}_4\text{CH}=\text{NCHR}-)_2][\text{BF}_4]_2$ ($\text{L} = \text{CO}$ or NCMe , and $\text{R} = \text{Ph}$ or H) (**Figure 1, E**) were reported by Sonnenberg and Morris, and were efficient at releasing hydrogen from ammonia-borane, in a process that was found to be heterogeneous in nature.³⁴ In 2014 Fe^{II} bis(phosphinite) hydride pincer complexes (see **Figure 1, F** for a selected example) were reported to release 2.3 – 2.5 equiv. of H_2 from $\text{H}_3\text{N}\cdot\text{BH}_3$ at 60 °C.³⁵ The σ -complex $[(\text{POCOP})(\text{FeH}(\kappa^1\text{-HBH}_2\cdot\text{NH}_3))]$ ($\text{POCOP} = [\kappa^3\text{-1,3-(OP}^t\text{Bu}_2)_2\text{C}_6\text{H}_3]$) was proposed as an intermediate based on NMR evidence. In addition, in 2015 Grützmacher reported a low-valent Fe complex, $\text{Na}[\text{Fe}(\text{trop}_2\text{dae})(\text{THF})_3]$ (**Figure 1, G**) ($\text{trop} = 5\text{H-dibenzo}[a,d]\text{cyclo-hepten-5-yl}$, $\text{dae} = (\text{NCH}_2\text{CH}_2\text{N})$), which proficiently dehydrocoupled $\text{Me}_2\text{NH}\cdot\text{BH}_3$ via the linear dimer intermediate **III**, with > 99% conversion after 4 h using 5 mol% loading at 25 °C.⁴² This work was continued using the related complex, $\text{Fe}(\text{trop}_2\text{dad})(\text{THF})$ ($\text{dad} = \text{diazadiene}$), which proficiently dehydrocoupled not only $\text{Me}_2\text{NH}\cdot\text{BH}_3$, but also $\text{MeNH}_2\cdot\text{BH}_3$ and $\text{H}_3\text{N}\cdot\text{BH}_3$.³⁷ Late in 2015, Schneider et al. published work using a Fe^{II} hydride complex, $\text{FeH}(\text{CO})(\text{PNP})$ ($\text{PNP} = \text{N}-(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2$) (**Figure 1, H**). The authors reported efficient $\text{H}_3\text{N}\cdot\text{BH}_3$ dehydrocoupling at room temperature, and proposed a homogeneous

mechanism which included amine-borane σ -complexes and ligand cooperation.³⁸ The related Fe hydride complex, (PNHP)Fe(H)(CO)(HBH₃) (PNHP = HN(CH₂CH₂P^{*i*}Pr₂)₂) was subsequently shown to catalyse the formation of high molecular weight poly(methylaminoborane) in under 24 h at 25 °C.⁴⁰ The mechanism was also proposed to be based around formation of an aminoborane intermediate via ligand cooperation.

A series of diiron complexes, (μ -SCH₂XCH₂S)(Fe(CO)₃)₂ (X = CH₂, CMe₂, CEt₂, NMe, *Nt*-Bu), has also been investigated as homogeneous amine-borane dehydrocoupling catalysts (**Figure 1, I**).³⁹ A new type of Fe(II) catalyst has also been reported, using the β -diketiminato ligand and a labile CH₂TMS co-ligand (**Figure 1, J**).⁴¹ It was shown to act as a highly efficient catalyst for the dehydrocoupling of a range of amine-boranes and phosphine-boranes.

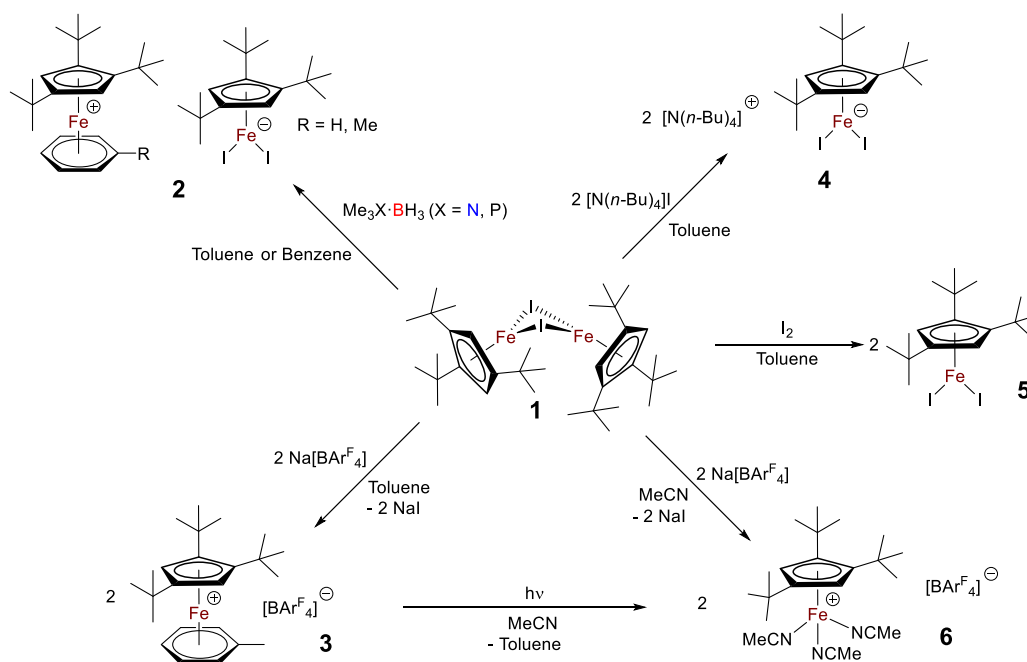
Herein, we report the synthesis of a range Fe^{II} and Fe^{III} complexes, containing the bulky Cp' (Cp' = η^5 -(1,2,4-*t*-Bu)₃C₅H₂) ligand,⁴² and an investigation of their reactivity with the amine-borane **I** as the substrate. The dehydrocoupling of the latter was selected for study due to the simplicity of the products involved, which facilitates mechanistic investigations.

Results

Synthesis and characterisation of complexes 1-6

We initially focused on the synthesis of a range of Fe complexes (**1-6**) containing the bulky 1,2,4-C₅H₂(*t*-Bu)₃ cyclopentadienyl (Cp') ligand as potential precatalysts for the dehydrocoupling of **I** (**Scheme 2**). The coordinatively unsaturated paramagnetic 16-electron dimeric iodo-bridged Fe(II) complex [Cp'FeI]₂ (**1**) was prepared as a red crystalline solid in 31% yield based on the reported reaction between NaCp' and FeI₂(THF)₂.⁴⁴ An excess of Me₃N•BH₃ was added to a toluene solution containing **1** in an attempt to yield a σ -borane complex of the type [Cp'Fe(κ^2 -H₂BH•NMe₃)]⁺. Precipitation of an air-sensitive yellow solid occurred after 18 h at 20 °C. Recrystallisation from a mixture of *o*-dichlorobenzene, THF and hexanes (1:1:3) at -40 °C gave single crystals suitable for an

X-ray diffraction study, which identified the product as the salt $[\text{Cp}'\text{Fe}(\eta^6\text{-Tol})][\text{Cp}'\text{FeI}_2]$ (**2**) (Tol = toluene) (**Figure 2**).⁴⁵ In the absence of the amine-borane, no formation of **2** was observed.



Scheme 3. Overview of Fe complexes synthesised from **1**.

The molecular structure of **2** contains a cationic Fe centre with an η^5 -bonded Cp' and an η^6 -bonded toluene moiety and an anionic Fe centre that is bonded to a η^5 -Cp' and two iodide ligands. Numerous examples of cyclopentadienyl Fe η^6 -aryl complexes are known, where UV irradiation can typically displace the aryl group, however there are no previous reports of a monomeric cyclopentadienyl Fe dihalide complex.⁴⁶⁻⁵⁰ The Tol(centroid)–Fe(1) distance of 1.564(1) Å was within the range of typical η^6 -aryl-Fe distances that can be found on the CCDC database (1.53–1.59 Å).⁵¹ By ^1H NMR spectroscopy, the *t*-Bu signals for the paramagnetic anion in **2** were found at -31.0 and -20.1 ppm. Whilst the cation has a valence electron count of 18, the significant downfield ^1H NMR shifts for the Cp' *t*-Bu (6.93 and 7.46 ppm), Cp'–H (21.5 ppm), and η^6 -Tol protons (Me: 10.9 ppm, Ar-H: 16.2, 29.7, and 32.6 ppm) are consistent with ion pairing interactions with the paramagnetic 16-valence electron anion (**Figure S1**).

Monitoring the reaction between an excess of $\text{Me}_3\text{N}\cdot\text{BH}_3$ and **1**, by ^1H and ^{11}B NMR spectroscopy in C_6D_6 provided tentative evidence for σ -complex formation. By ^1H NMR spectroscopy, the Me signal of the amine-borane was shifted downfield to 7.4 ppm relative to uncomplexed $\text{Me}_3\text{N}\cdot\text{BH}_3$, which is found at 2.6 ppm (in C_6D_6) (**Figure S2**). Furthermore, no ^{11}B NMR resonances were observed at 22 °C, which is unexpected considering a quartet resonance of -14 ppm is anticipated for $\text{Me}_3\text{N}\cdot\text{BH}_3$.⁵² After several days a yellow precipitate formed, which could be dissolved in THF-d_8 and was analysed by ^1H NMR spectroscopy. This revealed peaks at -30.34, -19.87, 8.86, 9.88 and 21.68 ppm consistent with formation of the complex $[\text{Cp}'\text{Fe}(\eta^6\text{-C}_6\text{D}_6)][\text{Cp}'\text{FeI}_2]$ (**Figure S3**), but also excess $\text{Me}_3\text{N}\cdot\text{BH}_3$ at 2.58 ppm. The initial interaction between an excess of **1** and $\text{Me}_3\text{N}\cdot\text{BH}_3$ was probed at low temperature in toluene- d_8 (**Scheme S5, S6**). Although no signal for $\text{Me}_3\text{N}\cdot\text{BH}_3$ could be detected by ^{11}B NMR at 25 °C, upon cooling to -80 °C a single broad peak at -5.5 ppm was observed and this was assigned to be free $\text{Me}_3\text{N}\cdot\text{BH}_3$. By ^1H NMR spectroscopy at 25 °C the Me signal was observed at 6.0 ppm but upon cooling to -80 °C it had shifted to 3.7 ppm.

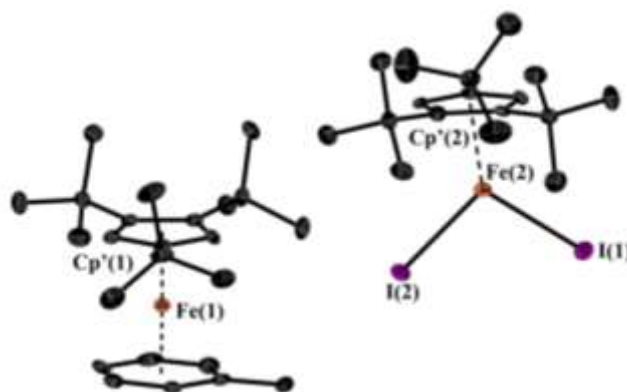


Figure 2. Molecular structures of the cation and anion in **2**. H atoms omitted for clarity; thermal ellipsoids depicted at the 50% probability level. Selected bond distances (Å) and angles (°): Cp'(1)–Fe(1) 1.687(1), Tol–Fe(1) 1.564(1), Cp'(2)–Fe(2) 1.989(1), Fe(2)–I(1) 2.7003(6), Fe(2)–I(2) 2.6144(6), I(1)–Fe(2)–I(2) 102.20(2).

The cation in **2** could be independently synthesised by the reaction between $[\text{Cp}'\text{FeI}]_2$ and 2 equivalents of $\text{Na}[\text{BAr}^{\text{F}}_4]$ ($\text{BAr}^{\text{F}}_4 = [\text{B}(\text{C}_6\text{H}_3(m\text{-CF}_3)_2)_4]$) in toluene, which yielded $[\text{Cp}'\text{Fe}(\eta^6\text{-Tol})][\text{BAr}^{\text{F}}_4]$ (**3**). Yellow single crystals could be isolated in 38% yield from CH_2Cl_2 at -40 °C and

allowed the molecular structure to be determined by X-ray diffraction (**Figure S7**). Compound **3** was characterised in solution by ^1H , ^{11}B , ^{13}C and ^{19}F NMR spectroscopy. The ^1H NMR spectrum (in CDCl_3) was characteristic of a diamagnetic species, where the *t*-Bu groups on Cp' were found as sharp singlets at 1.22 and 1.38 ppm (ratio 1:2), and the Cp'-H proton was assigned to a singlet resonance at 4.49 ppm (**Figure S8**). This contrasts with the ^1H NMR of the cation in **2**, which forms a tight ion pair with a paramagnetic anion, for which the Cp' *t*-Bu protons are downfield shifted (see above).

The paramagnetic anion in **2** could be independently synthesised by reacting 2 equivalents of $[\text{N}(n\text{-Bu})_4]\text{I}$ with **1** in toluene. Single crystals of $[\text{N}(n\text{-Bu})_4][\text{Cp}'\text{FeI}_2]$ (**4**) suitable for characterisation by single-crystal X-ray diffraction were obtained (For the molecular structure see **Figure 3, (a)**). The Fe–I bond length in **4** of 2.6343(4) and 2.6695(4) Å is comparable to the Fe–I bond length in the dimeric **1**, 2.6748(5) and 2.7088(5) Å.⁴⁴ By ^1H NMR spectroscopy, broad *t*-Bu signals were observed at -31.4 and -20.3 ppm, virtually identical to those in the ^1H NMR spectrum of the same anion in complex **2** (**Figure S13**). The ^1H NMR signals corresponding to the cation, $[\text{N}(n\text{-Bu})_4]^+$ at 5.06, 12.4, 24.4 and 34.0 ppm displayed no fine structure, and the resonances became increasingly broad as the downfield shift increased, suggestive of ion-pairing.

The neutral paramagnetic Fe^{III} diiodide complex $\text{Cp}'\text{FeI}_2$ (**5**) was obtained by oxidation of **1** by I_2 in pentane. Dark-green crystals of **5**, suitable for X-ray diffraction could be isolated in 46% yield from pentane at -40 °C (For the molecular structure see **Figure 3, (b)**). By ^1H NMR spectroscopy, the *t*-Bu groups were found at -10.4 and -13.7 ppm (**Figure S14**). As in the case for the other paramagnetic complexes **2/4**, the Cp–H signals were too broad to be observed, which is unsurprising considering the Cp–H resonance for the paramagnetic complex **1** was found to be very broad at 36.8 ppm ($\nu_{1/2} \sim 1800$ Hz).⁴³ As expected, the Fe–I bond lengths of 2.5286(5) and 2.5205(5) Å in the neutral complex **5** are shorter than those of the anionic Fe^{II} iodide complexes **2** and **4** (2.65 – 2.66 Å), and shorter than for the neutral Fe^{II} complex **1** (2.6748(5) and 2.7088(5) Å). The I–Fe–I bond angle of 103.8(2)° in **5** is slightly wider than for **4**, 95.7(1)°, which is expected based on the shorter Fe–I bond distance, which may lead to unfavourable steric interactions. Whilst it was possible to purify **5**, in solution this species

was found to decompose over the course of a week, as evidenced by the formation of black magnetic precipitate, presumably Fe metal.

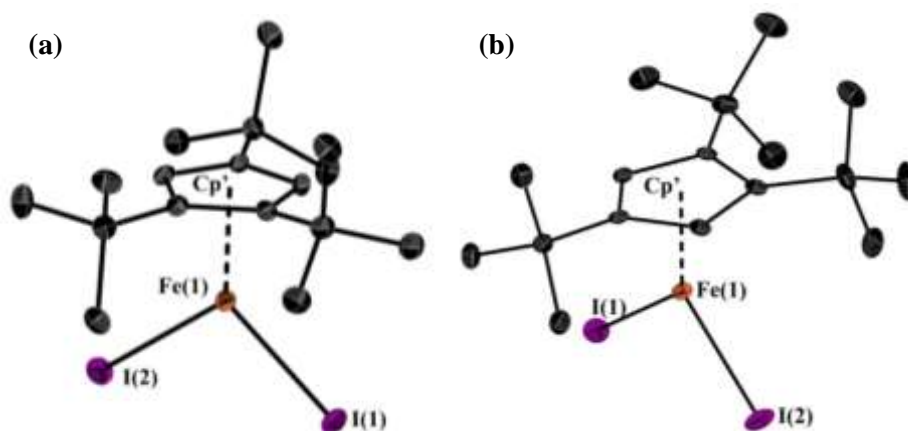


Figure 3. Molecular structures of the anion present in **4** (a) and the neutral species **5** (b). H atoms have been omitted for clarity; thermal ellipsoids depicted at the 50% probability level. $[N(n\text{-Bu})_4]^+$ in **4** has also been omitted for clarity. Selected bond distances (\AA) and angles ($^\circ$): (for **4**) $\text{Cp}'\text{-Fe(1)}$ 1.9765(4), Fe(1)-I(1) 2.6343(4), Fe(1)-I(2) 2.6695(4), $\text{Cp}'\text{-Fe(1)-I(1)}$ 131.77(2), $\text{Cp}'\text{-Fe(1)-I(2)}$ 127.28(2), I(1)-Fe(1)-I(2) 100.94(2); (for **5**) Fe(1)-I(1) 2.5286(5), Fe(1)-I(2) 2.5205(5), $\text{Cp}'\text{-Fe(1)}$ 1.8648(5), I(1)-Fe(1)-I(2) 103.81(2), $\text{Cp}'\text{-Fe(1)-I(1)}$ 127.07(2), $\text{Cp}'\text{-Fe(1)-I(2)}$ 128.99(2).

Walter and White previously reported that the complex $[\text{Cp}'\text{Fe}(\text{MeCN})_3][\text{PF}_6]$ could be obtained from the reaction of $[\text{Cp}'\text{FeI}]_2$ with 2 equivalents of $\text{Na}[\text{PF}_6]$ in MeCN.⁴⁴ We performed an analogous reaction using $\text{Na}[\text{BAR}^{\text{F}}_4]$, which yielded the purple diamagnetic complex $[\text{Cp}'\text{Fe}(\text{MeCN})_3][\text{BAR}^{\text{F}}_4]$ (**6**). Purple single crystals of **6** suitable for X-ray diffraction studies could be obtained in 65% yield by slow diffusion of hexanes into THF (see structure in **Figure 4**). Complex **6** could also be synthesised by the UV irradiation of **3** in MeCN at 20 $^\circ\text{C}$. The ^1H , ^{11}B , ^{13}C and ^{19}F NMR spectra in **6** were consistent with the assigned structure, based on previously reported data on the cation.⁴⁴ Furthermore, rapid exchange between free and bound MeCN ligands was observed on the NMR time scale in CD_2Cl_2 , which could be dramatically slowed by cooling the sample to -80 $^\circ\text{C}$ (**Figure S15**). Evidence for a similar exchange process has been reported previously.⁴⁴ In 2015 the Scheer group reported a crystallographically characterised example of the Fe cation, $[\text{Cp}^*\text{Fe}(\text{MeCN})_3]^+$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$). This

complex contained an average Fe–N bond length of 1.93 Å and a Cp*–Fe distance of 1.68 Å, which are similar to the analogous distances of 1.941(4) and 1.681(2) Å found for **6**.⁵³

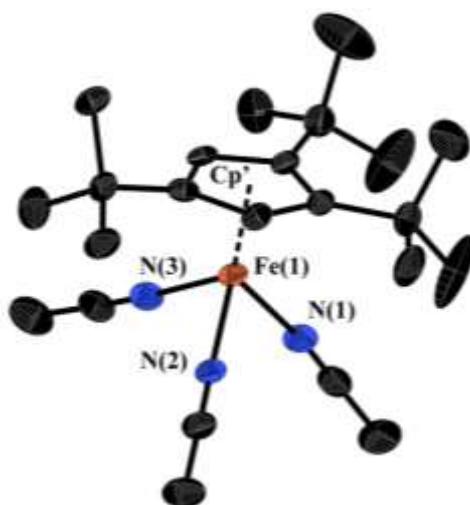


Figure 4. Molecular structure of the cation in **6**. H atoms, BAr^F₄ and THF have been omitted for clarity; thermal ellipsoids set at the 50% probability level. Selected bond distances (Å): Cp*–Fe(1) 1.681(1), N(1)–Fe(1) 1.941(4), N(2)–Fe(1) 1.938(4), N(3)–Fe(1) 1.944(4).

Electronic Structure of **4**

As NMR evidence indicated that the anion in **2** and **4** contained a paramagnetic Fe centre (high spin d⁶, *S* = 2), we examined the nature of electronic structure using magnetometry, electron paramagnetic resonance (EPR) spectroscopy and *ab initio* complete active space self-consistent field spin-orbit (CASSCF-SO) calculations. Given the likely coupling arising from presence of two distinct Fe species in **2**, we chose to limit our investigation to **4** for simplicity and as a result of only the anion being active catalytically (see below). The $\chi_M T$ product ($\chi_M T \approx \mu_{\text{eff}}^2/8$) for **4** at 300 K was found to be 3.4 cm³ mol^{−1} K, which is slightly higher than the value expected for a *S* = 2 state (high-spin d⁶) with *g* ≈ 2 of 3.0 cm³ mol^{−1} K, suggesting that *g* ≈ 2.13. $\chi_M T$ is fairly constant with decreasing temperature until 50 K where it decreases gradually to reach 2.4 cm³ mol^{−1} K at 2 K, likely due to zero-field splitting (ZFS) of the *S* = 2 ground state (**Figure 5**). Isothermal magnetization measurements approach a saturation value of 2.3 μ_B mol^{−1} (**Figure 5**), much lower than expected for a pure *S* = 2 state; this low value and coincidence of the 2 and 4 K data at high fields also suggest significant ZFS of the ground

state. Compared to the overlapping magnetization isotherms observed for similar pseudo-trigonal Fe^{II} complexes Fe(NHC)Br₂ (NHC = *N,N*-bis(2,6-diisopropylphenyl)imidazol-2-amidine) which directly evidenced a positive axial ZFS (i.e. $D > 0$),⁵⁴ the temperature dependence observed here suggests the opposite case with $D < 0$. Simultaneous fitting of the magnetic data with PHI⁵⁵ using the spin Hamiltonian (1) gives the best fit for $g = 2.114(2)$ and $D = -17(1) \text{ cm}^{-1}$ ($E = 0 \text{ cm}^{-1}$ fixed) (**Figure 5**).

$$\hat{H} = \mu_B g \hat{S} \cdot \vec{B} + D \left(\hat{S}_z^2 - \frac{1}{3} \hat{S}^2 \right) + \frac{1}{2} E \left(\hat{S}_+^2 + \hat{S}_-^2 \right) \quad (1)$$

EPR spectroscopy at X- and Q-band (ca. 9.4 and 34 GHz, respectively) and cryogenic temperatures with a solid state sample of **4** gave no resonances, suggesting a significant rhombic component to the ZFS (non-zero E). As Q-band was the highest frequency employed and no resonances were observed, this suggests that the gap between the lowest two states of the $S = 2$ multiplet is at least 1.1 cm^{-1} ; for $D = -17(1) \text{ cm}^{-1}$, this suggests that the rhombic ZFS parameter is $|E| \geq 3 \text{ cm}^{-1}$. Adding this term to the fit of the magnetic data does not provide better agreement with experiment; this is because the thermodynamic experiment is insensitive to a small rhombicity. *Complete Active Space Self Consistent Field – Spin Orbit* (CASSCF-SO) calculations (see Experimental section for details) suggest a ground $S = 2$ state with a reasonably low-lying first excited state (**Table S1**). This low-lying excited state is mixed into the ground state multiplet via SO coupling and is the source of significant magnetic anisotropy (**Table S2**). Expression of the CASSCF-SO ground multiplet as a pseudo-spin $S = 2$ suggests $g = 2.25$, $D = -42 \text{ cm}^{-1}$ and $E = 2 \text{ cm}^{-1}$; while the magnitude of D is clearly over estimated (a common feature of minimal active space calculations as employed here), the calculations agree with the magnetic data supporting a significant negative D with $g > 2$.

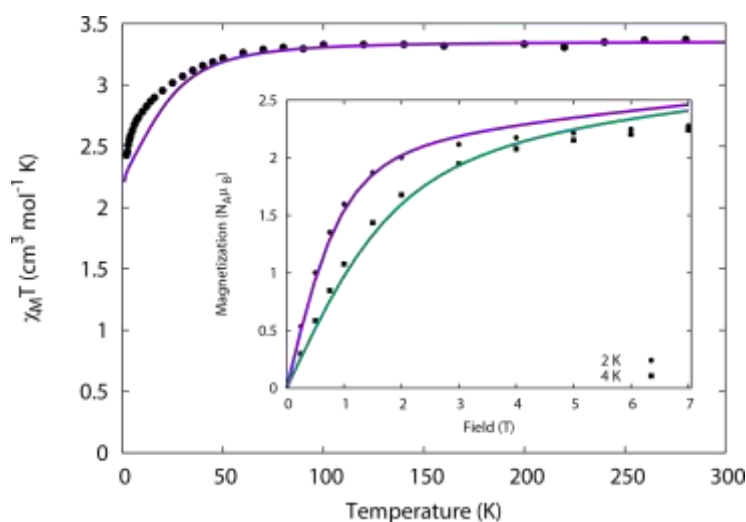
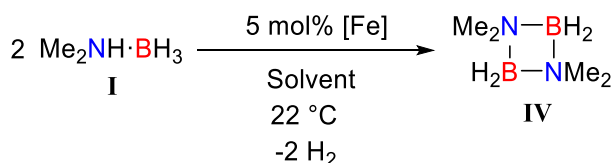


Figure 5. Magnetic susceptibility of **4** recorded under a 0.1 T field. Inset: Magnetization of **4** at 2 and 4 K. Lines are the best fit using Equation 1 with parameters $g = 2.114(2)$, $D = -17(1) \text{ cm}^{-1}$ and $E = 0 \text{ cm}^{-1}$.

Dehydrocoupling of **I** by precatalysts **1-6**

In order to make comparisons with the previously reported cyclopentadienyl Fe based precatalyst $\text{CpFe}(\text{CO})_2\text{I}$, which required photoirradiation, we explored the activity of **1-6** towards the dehydrocoupling of **I** in solution (**Table 1**). In a typical reaction, **I** was dissolved in either toluene or THF, and 5 mol% catalyst, **1-6** was added in a closed system under Ar. The reactions were monitored by ^{11}B NMR spectroscopy at 22 °C over 4 h (to allow a comparison with previous data³³ for $\text{CpFe}(\text{CO})_2\text{I}$ and related Fe species) and for up to 168 h (7 days) in the cases of less active precatalysts. (Table 1).

Table 1. Dehydrocoupling activity of various Fe complexes at 5 mol% loading towards **I** ([**I**] = 0.485 M).



Entry	[Fe] (5 mol%)	Solvent	Predominant intermediate	Time (h)	Yield of IV ^a (%)
1 ^d	1	THF (Tol)	II	4	20 (2)
2 ^d	1	THF (Tol)	II	168	48 (70)
3 ^d	2^c	THF	II	4	1
4 ^d	2^c	THF	II	66	22
5	3	THF	-	4	0
6	3^b	THF	II	4	17
7 ^d	4	THF	II	4	2
8 ^d	4	THF (Tol)	II	71	25 (82)
9 ^d	5	Tol	II	4	1
10	6	THF	III	4	54
11	6	THF	III	19	80
12	CpFe(CO) ₂ I ^b	THF (Tol)	III	4	30 (55)

^aYields calculated from ¹¹B NMR spectra using B(OⁱPr)₃ as an internal reference and no significant variation in the values was noted in a repeat experiment. Brackets refer to yield in toluene. ^bWith UV irradiation. ^cComplex **2** was insoluble in toluene. A concentration of 0.11 M of **I** was used. ^dYields determined by NMR are subject to a large uncertainty as a result of the presence of a broad background peak from the interaction of **I** with the paramagnetic iron centre.

(a) [Cp'FeI]₂ (**1**) as a precatalyst

Compound **1** features labile Fe–I bonds and exists in equilibrium with the mononuclear species Cp'FeI, as demonstrated by formation of (Cp'Fe)₂BrI from the mixing of stoichiometric amounts of [Cp'FeI]₂ and [Cp'FeBr]₂.⁴⁴ This is further indicated by the previous report of the facile reaction of **1** with CO at 25 °C, yielding the orange 18-electron complex Cp'Fe(CO)₂I.⁴⁴ Compound **1** therefore can be viewed as a source of the coordinatively unsaturated 14-electron Fe fragment Cp'FeI. Reactions with hydride sources have also been reported, where addition of K[Et₃BH] and H₂ to **1** yielded a mixture of [Cp'FeH₂]₂ and Cp'₂Fe₂H₃.⁵⁶ Furthermore, the reaction between **1** and Na[BH₄] led to formation of the borohydride complex Cp'Fe(BH₄) which converted to the BH₂ bridged cyclic trimer [Cp'FeBH₂]₃ with weak B–B bonds over a period of 10 days under ambient conditions.⁵⁶ Thus, the

reaction between **1** and **I**, which contains hydridic B–H bonds, was anticipated to proceed *via* coordination of one or more B–H bonds to the metal centre.

Addition of **I** to a C₆H₆ solution containing 5 mol% of **1** led to an immediate colour change from red to yellow (**Figure S17**), along with the evolution of gas (**Table 1, Entry 1,2**). Monitoring the reaction by ¹¹B NMR spectroscopy, immediately after mixing, revealed no observable peak associated with **I** (-15 ppm) (**Figure S19**). By repeating the reaction in toluene and cooling the sample to -70 °C, a broad ¹¹B NMR signal assigned to Fe-coordinated **I** appeared at -7.3 ppm (**Figure S21**). By ¹H NMR spectroscopy at 22 °C, the *t*-Bu resonances of the Cp' ligands were shifted downfield upon addition of **I** to **1** from -7.8 and -13.5 ppm to -3.2 and -5.9 ppm, respectively (**Figure S18**). Furthermore, the amine-borane methyl group was observed as a broad signal at 8.4 ppm, also suggestive of coordination of **I** to the paramagnetic Fe centre. On the basis of the significant downfield shift, we tentatively propose that a paramagnetic 16-electron Fe species featuring the σ-bound amine-borane, Cp'FeI(κ¹-HBH₂•NMe₂H) is the likely complex formed rather than a diamagnetic 18-electron Cp'FeI(κ²-H₂BH•NMe₂H) complex.

Continued monitoring by ¹¹B NMR spectroscopy over a period of 7 days in either toluene or C₆D₆ led to the observation of new signals assigned to the major product, cyclodiborazane **IV** (δ_B 4.1 ppm, t, ¹J_{BH} = 113 Hz) (yields estimated by NMR after 4 h and 168 h are given in Table 1),⁵⁸ aminoborane **II** (δ_B 36.5 ppm, ¹J_{BH} = 127 Hz), a minor product H₂B(η-H)(η-NMe₂)BH₂ (δ_B -17.6 ppm, dt, ¹J_{BH} = 129 Hz, 31 Hz)⁵⁹, and an unidentified broad minor peak at 22.1 ppm. Over the course of 7 days the reaction mixture darkened and a magnetic black solid precipitated, suggesting gradual reduction of **1** to Fe metal in the presence of **I**, coinciding with a reduction in the rate of formation of **IV**. Detection of aminoborane **II** contrasts with previous results using the precatalyst CpFe(CO)₂I where formation of **III** (δ_B -13.7 ppm (q, ¹J_{BH} = 94 Hz, BH₃), 1.4 ppm (t, ¹J_{BH} = 108 Hz, BH₂))⁶⁰ was detected as the major intermediate, suggesting that different dehydrocoupling mechanisms are operating. Furthermore, CpFe(CO)₂I was much more active leading to 54% conversion to **IV** after 4 h.³³

In order to establish whether the dehydrocoupling of **I** by **1** proceeded via a homogenous or heterogeneous mechanism, substoichiometric phosphine poisoning, and filtration experiments were performed.^{61,62} Previously, Fe-catalyzed dehydrocoupling of **I** with photoirradiated $\text{CpFe}(\text{CO})_2\text{I}$ was shown to proceed by a homogeneous mechanism, whereas the Fe^{I} dimers $[\text{CpFe}(\text{CO})_2]_2$ and $[\text{Cp}_2\text{Fe}_2(\text{CO})_3(\text{MeCN})]$ gave rise to Fe nanoparticles, which acted as heterogeneous catalysts.³² Filtration of a solution of 5 mol% **1** and **I** after 24 h with a 0.2 μm PTFE filter did not have a measurable effect on the reaction rate (**Figure S25**). Further evidence in support of a homogenous mechanism came from poisoning experiments, using phosphine coordination to block catalytic sites.⁶¹ Addition of 0.1 equiv. (with respect to **1**) of PMe_3 by microsyringe to a dehydrocoupling reaction of **I** with **1** (5 mol%) after 6 h did not cause the reaction to halt, consistent with a high concentration (> 0.5 mol%) of active sites, and indicative of a homogeneous process rather than a heterogeneous pathway involving Fe nanoparticles (**Figure S26**). The formation of Fe metal nanoparticles during the course of the dehydrocoupling reaction suggests reduction of complex **1** by **I** occurs competitively with dehydrocoupling, which is not surprising considering the substantial body of work on the reducing ability of amine-borane adducts.^{63,64} In contrast to $[\text{CpFe}(\text{CO})_2]_2$, where filtering or poisoning curtails catalysis implying an active role for heterogeneous Fe particles, the Fe metal particles generated from **1** do not appear to play a significant role in dehydrocoupling. Indeed, relatively large Fe particles ($R_h = 550$ nm) have been previously shown to be very poor dehydrocoupling catalysts, only resulting in ca. 1% conversion from **I** to **IV** after 24 h.³³

Attempts were made to isolate a more stable analogue of the initially formed σ -complex that is proposed to form in dehydrocoupling reactions between the Fe complex **1** and **I**. To this end, stoichiometric amounts of the tertiary amine-borane $\text{Me}_3\text{N}\cdot\text{BH}_3$, and the phosphine-borane $\text{Me}_3\text{P}\cdot\text{BH}_3$ were added separately to a solution of **1** in THF at 22 °C. As discussed above, when this reaction was performed with the former species in either C_6H_6 or toluene complex **2** was found to precipitate out of the reaction mixture. Analysis of the reaction mixture involving $\text{Me}_3\text{N}\cdot\text{BH}_3$ and **1** carried out in THF by ^{11}B NMR spectroscopy after 5 mins revealed a broad peak at 7.4 ppm, with no B–H coupling (**Figure S21**). The downfield chemical shift, compared to unbound $\text{Me}_3\text{N}\cdot\text{BH}_3$ ($\delta = -14$ ppm) is

consistent with literature values for other transition metal $\text{Me}_3\text{N}\cdot\text{BH}_3$ σ -complexes.^{17,65} The *in situ* ^{11}B NMR spectrum of the analogous addition of $\text{Me}_3\text{P}\cdot\text{BH}_3$ to **1** in THF revealed a broad peak at δ 19.7 ppm and two minor broad peaks at δ 5.58 and δ 79.3 ppm, which did not correspond to σ -complexes. By ^{31}P NMR spectroscopy only a broad peak at δ 82.5 ppm could be observed (**Figures S23, S24**), which was assigned to the known $[\text{Me}_3\text{PI}]^+$ cation.⁶⁶ Attempted isolation of intermediates from both the stoichiometric reactions involving $\text{Me}_3\text{R}\cdot\text{BH}_3$ ($\text{R} = \text{P}, \text{N}$) were unsuccessful, and crystallisation led to the isolation of **1**.

(b) $[\text{Cp}'\text{Fe}(\eta^6\text{-Tol})][\text{Cp}'\text{FeI}_2]$ (**2**), $[\text{Cp}'\text{Fe}(\eta^6\text{-Tol})][\text{BAR}^F_4]$ (**3**) and $[\text{N}(\text{n-Bu})_4][\text{Cp}'\text{FeI}_2]$ (**4**) as precatalysts

Addition of **I** to 5 mol% **2** in THF led to dehydrocoupling yielding **IV** (22% after 66 h), again via the intermediate **II** (**Table 1, Entry 3,4**). In principle, complex **2** featuring both an Fe containing cation and anion, has the potential for dehydrocoupling reactions to occur at either/both metal centres. To resolve this issue, **3** and **4** were also investigated as precatalysts, as these represented isolated forms of the cation and anion in **2**. Under ambient conditions complex **3** dissolved in THF showed minimal reactivity with **I** (0% conversion to **IV** after 4 h and only a trace of the latter was formed after 69 h), but upon UV irradiation, dehydrocoupling to form **IV** proceeded much faster (17% conversion after 4 h), via the intermediate **II** (**Table 1, Entry 5,6**). When UV irradiation was removed, the rate of dehydrocoupling returned to a minimal level. In contrast, complex **4** reacted with **I** at 22 °C in the absence of UV irradiation, yielding a yellow solution, followed by formation of **IV** via the intermediate **II** (**Table 1, Entry 7,8**) (25% conversion after 71 h). When toluene was used as a solvent, the dehydrocoupling rate increased (82% conversion after 71 h). A second loading of **I** could be added to the yellow solution (after 144 h) which led to further dehydrocoupling (**Figure 6**) without a further colour change. This contrasts to the case of complex **1**, which was found to be inactive towards additional **I**, presumably due to formation of metallic iron.

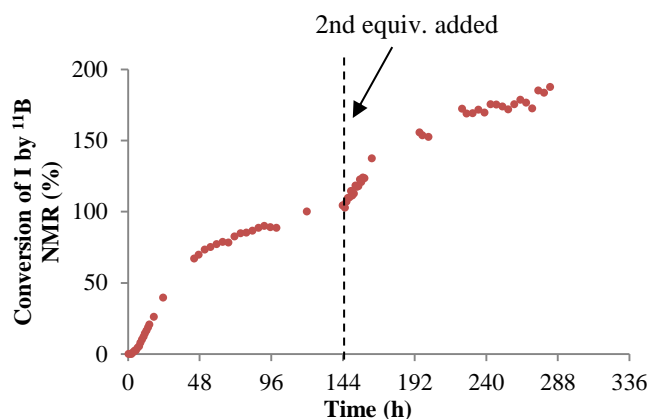


Figure 6. Reaction profile for the formation of **IV** from the dehydrocoupling of **I** (0.49 M) with the precatalyst **4** (5 mol%) in toluene, at 22 °C. A second loading of **I** (0.34 mmol) was added after 144 h.

(c) *Cp'FeI₂ (5) as a precatalyst*

Although an increasing number of Fe precatalysts have been recently reported for amine-borane dehydrocoupling, including a homogenous Fe^I precatalyst,^{36,37} no examples of an Fe^{III} precatalyst are currently known. With this in mind **I** was reacted with 5 mol% of **5** at 22 °C in toluene, whereby an immediate colour change was observed from green to yellow (**Table 1, Entry 9**). After mixing, the ¹¹B NMR spectrum showed a very broad signal at 45.8 ppm, as well as a trace amount of **IV** (< 1 %), and an unassigned triplet at -13.1 ppm (¹J_{BH} = 131 Hz) (**Figure S29**). Over the course of 20 h, the peak at -13.1 ppm decreased in intensity to zero, whilst at the same time a new peak at -17.6 ppm, assigned as H₂B(η-H)(η-NMe₂)BH₂,⁵⁹ emerged. After 2 days, the colour changed from yellow to pink but the conversion to **IV** did not proceed any further which indicated that **5** is a poor precatalyst for dehydrocoupling of **I**.

(d) [*Cp'Fe(MeCN)₃][BAR^F₄]* (**6**) as a precatalyst

An alternative approach to accessing open coordination sites for substrate binding and catalysis is to use labile ligands, which can be displaced by the substrate without the need for UV irradiation. This approach was taken with complex **6**, which contains labile MeCN ligands.⁴⁴ Upon addition of **I** to a solution of 5 mol% **6** in THF-d₈, the colour immediately changed first from purple to blue, and then darkened after 10 mins (**Table 1, Entry 10, 11**) (**Figure S30**). The conversion of **I** to **IV** via the

intermediate **III** after 4 h and 15 h was 54% and 80%, respectively, and indicated that **6** represents the most active of the precatalysts investigated in this report (**Figure 7**). By ^{11}B NMR spectroscopy, in addition to **III** (δ_{B} -13.7 (q, $^1J_{\text{BH}} = 94$ Hz, BH_3) and 1.4 (t, $^1J_{\text{BH}} = 108$ Hz, BH_2)⁶⁰ and **IV** (δ_{B} 4.1 ppm, t, $J_{\text{BH}} = 113$ Hz),⁵⁸ $\text{HB}(\text{NMe}_2)_2$ (δ_{B} 28.5 ppm, d, $J_{\text{BH}} = 124$ Hz),⁵⁹ and the boronium cation $[\text{BH}_2(\text{NHMe}_2)_2]^+$ (δ_{B} -2.8 ppm, t, $J_{\text{BH}} = 113$ Hz)⁶⁷ were also observed (**Figure S31**). Furthermore, slightly upfield of the BH_2 resonance for **III** was found a minor peak at 0.03 ppm (t, $^1J_{\text{BH}} = 110$ Hz), which we tentatively assign to the reported cyclic triborazane, $[\text{Me}_2\text{NBH}_2]_3$,⁶⁸ which is proposed to be present in a number of dehydrocoupling reactions.^{69,70} Due to the similarities in rate and products observed to dehydrocoupling, using $\text{CpFe}(\text{CO})_2\text{I}$ as a precatalyst, the reaction mediated by compound **6** was investigated in further detail. When C_6H_6 was used as a solvent rather than THF, no dehydrocoupling was detected by ^{11}B NMR after 3.5 days. However, after addition of a drop of THF, formation of **IV** was observed. Dehydrocoupling was also not detected in CH_2Cl_2 , despite an instantaneous colour change from purple to blue upon addition of **I**. Consistent with previous findings, **6** decomposed over a period of a week in CH_2Cl_2 to give black Fe metal.⁴⁴ When MeCN was used as a solvent, no dehydrocoupling was detected by ^{11}B NMR after 5 days.

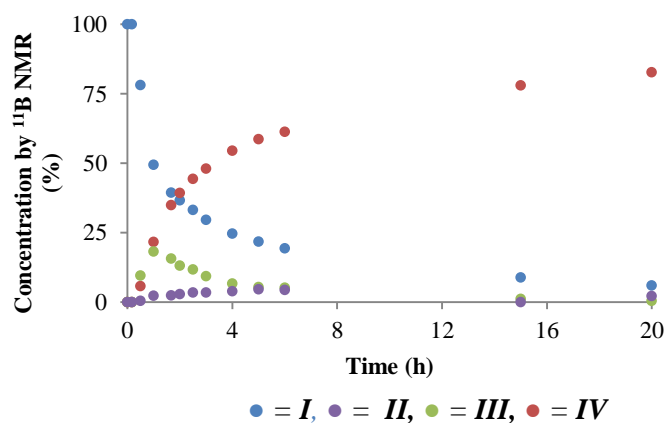


Figure 7. Reaction profile for the formation of **IV** from the catalytic dehydrocoupling of **I** (0.49 M), via **III** by 5 mol% precatalyst **6** at 22 °C, as monitored by $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, THF-d_8).

Further investigation of the dehydrocoupling reactions involving 5 mol% **6** in THF-d_8 by ^1H and ^{11}B NMR spectroscopy led to further insight into the reaction mechanism. Immediately after mixing, the ^{11}B NMR spectrum displayed 2 resonances at room temperature, one at -7.5 ppm assigned to $[\text{BAr}^{\text{F}}_4]^-$

and a broad peak at -11.9 ppm due to **I**, shifted downfield relative to the expected quartet. In some cases a peak at 21.4 ppm could also be observed, which is tentatively assigned as a σ -complex between **I** and **6**. Downfield ^{11}B NMR shifts relative to the free ligand have also been noted in the case of phosphine-borane coordination to Cp^*Ru centers.⁷¹ By ^1H NMR spectroscopy obvious differences occurred in the hydride region where the number of signals increased with time. Initially, there were predominantly two broad signals at -16.7 and -12.8 ppm (**Figure S33, S34**), however after 10 minutes the number of resonances in this region increased dramatically. Addition of **I** to 5 mol% **6** in CH_2Cl_2 led to a colour change purple to blue, however unlike when THF was used as a solvent, no dehydrocoupling was observed. Nonetheless variable temperature NMR spectroscopic analysis of CD_2Cl_2 solutions of 5 mol% **6** and **I**, revealed that upon cooling to -80°C , two hydride signals appeared in the ^1H NMR spectrum at -14.0 and -15.2 ppm (**Figure S39, S40**). The nature of dehydrocoupling process involving precatalyst **6** was explored through addition of a substoichiometric amount of PMe_3 . Addition to a dehydrocoupling reaction involving **I** and 5 mol% **6** after 2 h 40 mins (**Figure S35**) led to no significant change in the rate of conversion to **IV** which is consistent with a homogeneous process (**Figure S36**).

To investigate the minimum number of labile ligands required for catalytic dehydrocoupling of **I** to occur, the related known complexes $[\text{Cp}^*\text{Fe}(\text{CO})(\text{MeCN})_2][\text{PF}_6]$ (**7**) ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) and $[\text{Cp}^*\text{Fe}(\text{CO})_2(\text{MeCN})][\text{PF}_6]$ (**8**) were synthesised.⁷² Complex **7** was found to dehydrocouple **I** in THF at a catalyst loading of 5 mol%, yielding 46% of **IV** after 4.5 days. However complex **8**, which contains only a single labile ligand, showed no evidence of dehydrocoupling at a catalyst loading of 5 mol%. This is consistent with the previous report on complexes $[\text{CpFe}(\text{CO})_2\text{THF}][\text{SbF}_6]$, which also contained only one labile ligand, but which required UV light for dehydrocoupling of **I** to proceed.³³

The reaction between **III** and 5 mol% of **6** was carried out to further investigate the second step of the dehydrocoupling of **I** by **6**. It was found that the reaction led to 80% conversion to **IV** over the course of 6.5 h based on monitoring the reaction by ^{11}B NMR spectroscopy (**Figure 8 and S36**). Initially a small amount of **II** was formed (< 5%), which disappeared after 3 h. Furthermore, **I** (< 5%) was also observed suggesting conversion of **III** back to **I** and **II**. The formation of **I** and **II** via the

fragmentation of **III** has previously been reported under catalytic conditions when using $\text{Ir}(\text{POCOP})\text{H}_2$.⁷³

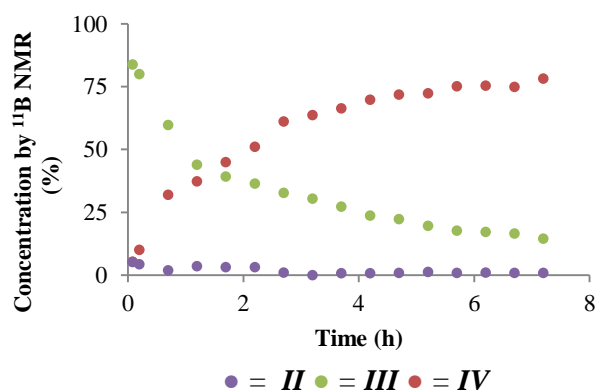
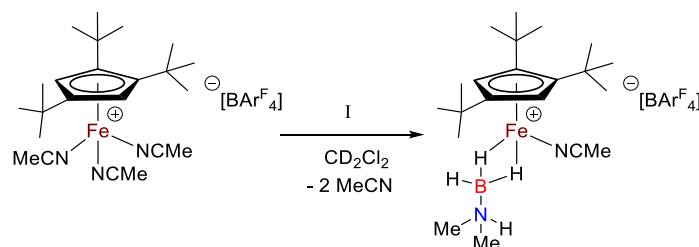


Figure 8. Reaction profile for the formation of **IV** from the catalytic dehydrocoupling of **III** (0.49 M) by 5 mol% precatalyst **6** in THF-d_8 at 22 °C, as monitored by $^{11}\text{B}\{^1\text{H}\}$ (96 MHz, THF-d_8) NMR spectroscopy.

ESI-MS analysis under anaerobic conditions was used in an attempt to provide further evidence for the formation of a σ -complex between **I** and **6**, since NMR evidence was inconclusive (**Figures S41, S42**).⁷⁴ An excess of **I** was added to a CH_2Cl_2 solution of **6** forming a blue solution which was analysed after 5 minutes by ESI-MS where a peak with a m/z of 389 Da, and an isotope pattern corresponding to the formula $\text{C}_{21}\text{H}_{42}\text{B}_1\text{Fe}_1\text{N}_2$ was detected. This is consistent with the presence of the cationic complex $[\text{Cp}'\text{Fe}(\text{MeCN})(\kappa^2\text{-H}_2\text{BH}\cdot\text{NMe}_2\text{H})]^+$ (**Scheme 4**). A second major peak at $m/z = 348$ Da, corresponding to $\text{C}_{19}\text{H}_{39}\text{B}_1\text{Fe}_1\text{N}_1$ was also present, consistent with the loss of MeCN to give the cation $[\text{Cp}'\text{Fe}(\kappa^2\text{-H}_2\text{BH}\cdot\text{NMe}_2\text{H})]^+$. Similar results, indicating formation of a σ -complex could be obtained from the reaction between excess $\text{DMAP}\cdot\text{BH}_3$ ($\text{DMAP} = 4\text{-dimethylaminopyridine}$) and **6** in CH_2Cl_2 , where mass peaks at $m/z = 466$ Da ($[\text{Cp}'\text{Fe}(\text{MeCN})(\kappa^2\text{-H}_2\text{BH}\cdot\text{DMAP})]^+$) and 425 Da ($[\text{Cp}'\text{Fe}(\kappa^2\text{-H}_2\text{BH}\cdot\text{DMAP})]^+$) were observed (**Figure S43, S44**). However in the case of $\text{DMAP}\cdot\text{BH}_3$, a major peak at $m/z = 547$ Da was also identified, consistent with assignment of the complex $[\text{Cp}'\text{Fe}(\text{DMAP})(\kappa^2\text{-H}_2\text{BH}\cdot\text{DMAP})]^+$. A linear diborazane σ -complex could also be detected by mixing

a CH_2Cl_2 solution of $\text{Me}_3\text{N}\cdot\text{BH}_2\text{NMe}_2\cdot\text{BH}_3$ and **6** for which a peak with $m/z = 460$ Da was recorded, consistent with the complex $[\text{Cp}'\text{Fe}(\text{MeCN})(\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_3)]^+$ (**Figure S45**). Attempts to crystallise the products from these reactions were unsuccessful, and yielded crystals of **6** or the amine-borane adducts.

The use of ESI-MS to analyse the dehydrocoupling reaction mixture of **I** and 5 mol% of **6** in THF after 22 h also revealed some interesting results (**Figure S46**). In contrast to the case immediately after mixing **I** and **6**, no peaks corresponding to either $[\text{Cp}'\text{Fe}(\text{MeCN})(\text{H}_3\text{B}\cdot\text{NMe}_2\text{H})]^+$ or $[\text{Cp}'\text{Fe}(\text{MeCN})(\text{H}_3\text{B}\cdot\text{NMe}_2\text{BH}_2\cdot\text{NMe}_2\text{H})]^+$ were detected. Instead, signals with isotope patterns indicating the presence of two Fe centres were detected between 600 and 680 Da, with a major peak at $m/z = 678$ Da with an isotope pattern consistent with the presence of two Cp'Fe fragments together with $\text{Me}_2\text{NH}\cdot\text{BH}_3$ and MeCN. Binuclear complexes have been previously isolated from dehydrocoupling reactions in the case of mononuclear Rh precatalysts and have also been postulated as intermediates.^{7,75-77}



Scheme 4. Proposed σ -complex formed by the reaction between **6** and **I**.

Discussion

Key differences were detected in the catalytic dehydrocoupling activity of **1-6** towards **I**. For precatalysts **1-4** the reaction proceeded by intermediate **II** rather than **III** and UV irradiation was necessary in the case of **3**. Precatalysts **1-4** were found to be considerably less active than **6**, whereas **5** was virtually inactive. Complex **6** possessed similar activity to our previously reported precatalyst $\text{CpFe}(\text{CO})_2\text{I}$ and also involved intermediacy of **III**.³³ Initial complexation between **6** and **I** likely forms a σ -complex $[\text{Cp}'\text{Fe}(\text{MeCN})(\kappa^2\text{-H}_3\text{B}\cdot\text{NMe}_2\text{H})]^+$ based on ^1H and ^{11}B NMR and ESI-MS

evidence. The amine-borane is substitutionally labile, as highlighted by VT NMR experiments, and the formation is apparently prevented by excess MeCN based in the absence of catalytic dehydrocoupling activity when this is used for the solvent. NMR evidence in the reaction of 5 mol% of **6** with **I** in d⁸-THF points towards the likely importance of Fe hydrides in the dehydrocoupling reaction. This is highlighted by the observation that no dehydrocoupling occurs in the initial stages of the reaction, when the proposed σ -complex $[\text{Cp}'\text{Fe}(\text{MeCN})(\kappa^2\text{-H}_3\text{B}\cdot\text{NMe}_2\text{H})]^+$ is present. As the reaction progressed and dehydrocoupling proceeded, it was not clear which if any of the many hydride signals detected by ¹H NMR, corresponded to active catalytic species. The key involvement of metal based hydrides in metal-catalysed amine-borane dehydrocoupling chemistry has been recently highlighted.⁴ Especially relevant was the recent isolation of the Fe hydride dimer, $[\text{LFeH}]_2$ (L = β -diketiminato) which was postulated to be important in the dehydrocoupling mechanism for $\text{Me}_2\text{NH}\cdot\text{BH}_3$.⁴¹ Furthermore, the cation $[\text{BH}_2(\text{NHMe}_2)_2]^+$ detected by ¹¹B NMR in the catalytic reaction of **6** with **I** has been previously reported to be formed from a σ -amine-borane complex as precursor in a mechanism involving the generation of active metal hydrides.⁶⁶ ESI-MS evidence provided further evidence that the cationic σ -complexes are precatalysts rather than active catalytic species. In the early stages of the reaction between **6** and **I** no dehydrocoupling occurred, only the cationic amine-borane σ -complexes were detected by ESI-MS. Once dehydrocoupling started cationic σ -complexes were no longer detected and the presence of cationic dimeric Fe species was observed. It should be noted, however, the involvement of neutral compounds as active species, which would not have been detected by ESI-MS, cannot be ruled out at this stage.

Summary

The use of amine-borane dehydrocoupling catalysts based on earth abundant metals is still a relatively unexplored field. The sterically demanding Cp' ligand has been used as a key structural component of the Fe complexes **1-6**, which have been studied as precatalysts for the dehydrocoupling of **I**. The electronic structure of the unusual paramagnetic $[\text{Cp}'\text{FeI}_2]^-$ anion, present in novel complexes **2** and **4**, has been investigated by SQUID magnetometry, EPR spectroscopy and *ab initio* CASSCF-SO

calculations, which all suggest a large negative ZFS of the ground $S = 2$ state with a significant rhombic component. Compounds **1**, **2**, **4** and **6** were found to catalyse conversion of **I** to **IV** at 22 °C, however complex **3** required UV irradiation for dehydrocoupling to occur. The aminoborane **II** was observed as the dominant intermediate in the reactions involving **1-4**, whilst **III** was the predominant intermediate for **6**, which was the most active precatalyst. Phosphine poisoning experiments in the latter case supported a homogenous process and ESI-MS evidence supported the initial formation of an amine-borane σ -complex, $[\text{Cp}^*\text{Fe}(\text{MeCN})(\kappa^2\text{-H}_2\text{BH}\cdot\text{NMe}_2\text{H})][\text{BAr}^{\text{F}}_4]$. However, these σ -complexes are likely to be precursors to the formation of Fe hydrides in the case of **6**, as evidenced by ^1H NMR spectroscopy. The identification of the true active homogeneous catalyst species in the dehydrocoupling of **I** by **6** (and indeed by $\text{CpFe}(\text{CO})_2\text{I}$) remains a key target. On the basis of this work, these reactions are likely to involve the intermediacy of Fe hydrides.

Associated Content

X-ray crystallographic information and all other analytical data. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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